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Remediation of groundwater contaminated with arsenic through enhanced natural attenuation: Batch and column studies

Saeedreza Hafeznezami [a, *], Amity G. Zimmer-Faust [a], Dukwoo Jun [a], Megyn B. Rugh [a], Heather L. Haro [a], Austin Park [a], Jae Suh [a], Tina Najm [a], Matthew D. Reynolds [b], James A. Davis [c], Tarannom Parhizkar [d], Jennifer A. Jay [a]

[a] Department of Civil and Environmental Engineering, University of California, Los Angeles 5732 Boelter Hall, Box 951593, Los Angeles, CA 90095, USA
[b] Drumlin Environmental, LLC, 97 India Street, Portland, ME 04101, USA
[c] Earth Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA
[d] Department of Material Science and Engineering, University of California, Los Angeles, 410 Westwood Plaza, Los Angeles, CA 90095, USA

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ABSTRACT

Batch and column laboratory experiments were conducted on natural sediment and groundwater samples from a contaminated site in Maine, USA with the aim of lowering the dissolved arsenate [As(V)] concentrations through chemical enhancement of natural attenuation capacity. In batch factorial experiments, two levels of treatment for three parameters (pH, Ca, and Fe) were studied at different levels of phosphate to evaluate their impact on As(V) solubility. Results illustrated that lowering pH, adding Ca, and adding Fe significantly increased the sorption capacity of sediments. Overall, Fe amendment had the highest individual impact on As(V) levels. To provide further evidence for the positive impact of Ca on As(V) adsorption, isotherm experiments were conducted at three different levels of Ca concentrations. A consistent increase in adsorption capacity (26–37%) of sediments was observed with the addition of Ca. The observed favorable effect of Ca on As(V) adsorption is likely caused by an increase in the surface positive charges due to surface accumulation of Ca^{2+} ions. Column experiments were conducted by flowing contaminated groundwater with elevated pH, As(V), and phosphate through both uncontaminated and contaminated sediments. Potential in-situ remediation scenarios were simulated by adding a chemical amendment feed to the columns injecting Fe(II) or Ca as well as simultaneous pH adjustment. Results showed a temporary and limited decrease in As(V) concentrations under the Ca treatment (39–41%) and higher levels of attenuation in Fe(II) treated columns (50–91%) but only after a certain number of pore volumes (18–20). This study illustrates the importance of considering geochemical parameters including pH, redox potential, presence of competing ions, and sediment chemical and physical characteristics when considering enhancing the natural attenuation capacity of sediments to mitigate As contamination in natural systems.

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1. Introduction

Arsenic (As) is a ubiquitous toxic element with known negative health effects for humans and a prominent environmental cause of cancer mortality worldwide (Duker et al., 2005; Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). The United States Environmental Protection Agency (USEPA) adopted the maximum contaminant level (MCL) of 10 μg/L for As in drinking water in accordance with the World Health Organization (WHO) guideline (EPA, 2002; WHO, 1993). Mobilization of naturally occurring As from the host solid phases into aqueous phase is a major environmental pollution problem on a global scale (Ng et al., 2003). The release of As can take place via dissolution processes such as oxidative weathering of As sulfide minerals and reductive dissolution of iron (Fe) oxides and hydroxides. Fig. 1 (based on work of Polizzotto et al., 2006) shows a simplified illustration of naturally occurring processes that can cause mobilization and release of As from solid into solution phase. In oxidizing systems, where As is primarily present as the oxidized form arsenate As(V), the main mechanism of mobilization is the alkaline desorption caused by the

* Corresponding author.
E-mail address: Saeedreza@ucla.edu (S. Hafeznezami).

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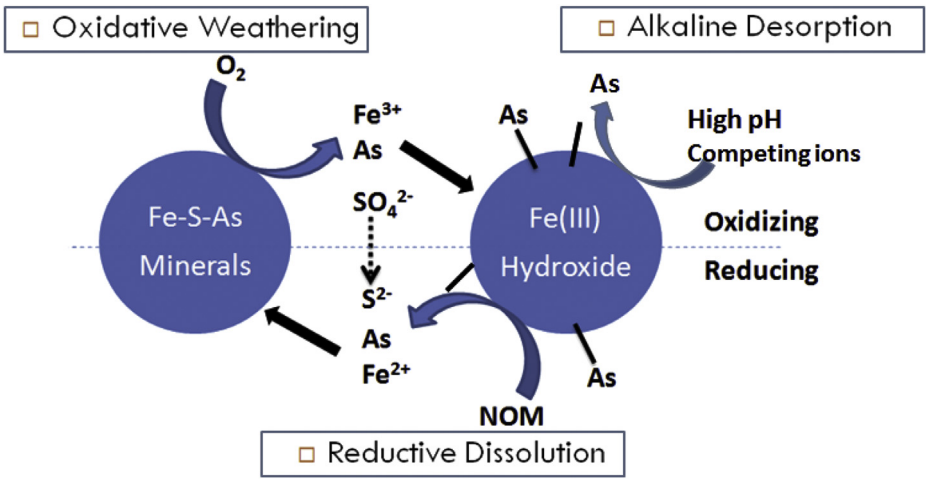

Fig. 1. Schematic representation of As mobilization and sorption mechanisms in subsurface environments.

increased repulsion between the negatively charged As(V) oxyanions and the higher negative charge of solid surfaces caused by increase in pH values (Nicolli et al., 2012; Ghosh et al., 2006; Genç-Fuhrman et al., 2004; Ayotte et al., 2003). Factors including presence of competing ions such as phosphate, persistence of high pH values, and natural pH buffering of solid phases, inhibit the sorption of mobilized As(V) and can lead to enriched As concentrations in groundwaters.

Arsenate adsorption and desorption in the environment is affected by a number of geochemical factors. At lower pH, arsenate adsorption is significantly higher due to the increase in net positive charge of the surface attracting negatively charged As(V) species.

Desorption processes can caused by the loss of adsorptive capacity of Fe oxide phases due to aging and transformation to more crystalline phases over time (Kumpiene et al., 2012).

Various human activities can also facilitate the mobilization of naturally occurring arsenic into groundwater resources. These activities include agricultural practices (Farooq et al., 2010), mining (Zhang et al., 2002), sewage disposal (Nickson et al., 2005), and aquaculture (Harvey et al., 2006).

Conventional methods for remediation of contaminated groundwaters generally involve a form of above-ground pump and treat system. These methods include oxidation, coagulation/filtration, ion exchange, adsorption media, and membrane filtration (EPA, 2002).

However, these systems usually involve high costs for installation and maintenance and the reduction of contaminant concentrations over the long term is not guaranteed (Martin and Kempton, 2000). Other methods, including in-situ remediation with a focus on promoting natural processes for retention of As and other contaminants, have increased in popularity in recent decades (Cundy et al., 2008; Cheng et al., 2009).

Sorption to solid phases is the main mechanism applicable to in-situ remediation of As contaminated groundwaters (Mohan and Pittman, 2007; Sharma and Sohn, 2009; Mondal et al., 2013). Solid phases include oxides and hydroxides of Fe, Al, Mn, clay minerals, and organic matter (Wang and Mulligan, 2006). Affinity of the natural adsorbents for retention of As in subsurface environments depends on various factors including surface properties, As speciation, pH and redox conditions, and presence of competing ions (Smedley and Kinniburgh, 2002).

Studies have shown the important role that Fe oxides present in soils and sediments take in immobilizing released As (Savage et al., 2000; Morin et al., 2002; Yang et al., 2002; Cances et al., 2005). The abundance and characteristics of Fe oxides present in soils and sediments can influence the mobility and transport of As both vertically and horizontally. Notably, adsorption of As on Fe oxides such as green rust, goethite, and lepidocrocite is orders of magnitude greater than adsorption by clays and feldspars (Lin and Puls, 2003). The sorptive oxide phases exist as either discrete minerals or more commonly as coatings on other minerals and solid particles (Singer et al., 2013). Accordingly, addition of Fe bearing chemicals to increase the sorption capacity of solid phases has been commonly used as a remediation strategy for immobilizing As and other contaminants in subsurface environments (Komárek et al., 2013).

Ferric salts have shown promising results in removing As from contaminated waters (Choong et al., 2007). Application of Fe oxides or their precursors as amendments for chemical stabilization of As in soils has been reported in the literature (Komárek et al., 2013; Kumpiene et al., 2008). Salts such as Fe (II)/(III) sulfates, or elemental Fe(0) have been used to control As mobility in soils by formation of insoluble secondary Fe-As minerals (e.g., scorodite, $FeAsO_4 \cdot H_2O$) and more importantly sorption onto precipitated Fe oxide minerals such as goethite and ferrihydrite. There have been a few attempts to remediate As through use of in-situ methods and application of Fe to increase sorption capacity of aquifers (Martin and Kempton, 2000; Welch et al., 2003; Paul et al., 2010). Martin and Kempton (2000) used ferrous sulfate and oxygenated solutions to form adsorptive coating in sand packed columns which delayed the breakthrough of As(V) by 30 pore volumes. The reactant solutes in that study were injected sequentially in order to avoid precipitation of Fe oxide phases at the injection port.

Paul et al. (2010) conducted laboratory column experiments as part of a remediation study to evaluate the effect of aeration, Fe(II) addition, and pH adjustment on levels of As in the effluent. In that study with application of 7 mg/L of Fe(II), As concentration was reduced from about 30 μg/L to below drinking water MCL after 30 pore volumes. Welch et al. (2003) utilized addition of ferric chloride ($FeCl_3$) as well as lowering pH in order to cause precipitation of hydrous ferric oxide (HFO) and facilitate As(V) adsorption. The study found very effective removal rates of As in laboratory experiments by combination of lowering the pH and increasing the iron oxide content; however, this practice resulted only in moderate As removal in the field due to local hydraulics of the aquifer and reaction kinetics. Application of Fe salts will also cause acidification of treated systems. This effect is especially noteworthy for application in oxidizing aquifers that are under alkaline conditions and

lowering the pH would be desirable for optimum adsorption of As(V).

While the solid phases significantly influence As oxyanion sorption, the composition of the solution phase also has important effects on the fate and transport of soluble As. Competition of solutes such as phosphate anion with As species for available sorption sites on a variety of surfaces has been well documented (Manning and Goldberg, 1996; Jain and Loeppert, 2000; Gao and Mucci, 2001; Hongshao and Stanforth, 2001; Liu et al., 2001; Goldberg, 2002; Violante and Pigna, 2002; Zeng et al., 2007; Zhang and Selim, 2008). On the other hand, cations such as Ca^{2+} have been reported by some to increase As adsorption on surfaces through increasing the positive charge on oxide surfaces (Wilkie and Hering, 1996; Meng et al., 2000; Masue et al., 2007; Currell et al., 2011). This phenomenon could be exploited in order to increase the adsorption on solid surfaces and overall natural attenuation of As in subsurface environments. To our knowledge, application of Ca^{2+} as an amendment chemical for immobilizing As in subsurface environments has not been tested.

Despite the fact that As-contaminated groundwater is a major global environmental problem, investigations on in-situ techniques for remediation are still lacking. Injection of reactants into the aquifer matrix for the purpose of enhancing the attenuation of soluble contaminants is a remediation approach that deserves further investigation and is the subject of this study.

While there are numerous published studies investigating the sorption of As on various pure and synthetic solid phases under varied conditions, only a limited number of studies based on conditions in real polluted aquifers have been conducted. This has led to a lack of environmentally relevant data for application of enhanced natural attenuation strategies on heterogeneous solid phases.

In this study, sediment and groundwater samples collected from a contaminated site in New England, USA were used in batch and column experiments to test the effectiveness of chemical amendments for enhancing natural attenuation of As(V).

Our overall hypothesis was that addition of Fe and Ca to the aqueous phase alongside pH adjustment is capable of increasing the natural attenuation of As(V) by providing more sorption sites and enhancing adsorption. The objectives were to: 1) determine the best treatment combination most likely to lead to increase As(V) attenuation (by conducting factorial batch experiments); 2) investigate the effects of Ca and pH adjustment (by conducting batch adsorption isotherm and acidification experiments); and to 3) simulate contamination and remediation scenarios conducting column experiments with sediments from locations within and outside known bounds of the contaminant plume.

2. Material and methods

The experimental work described here was conducted on sediment samples collected from various locations within the study site in order to gain overall understanding on effectiveness of different methods used to enhance the natural attenuation of As. Due to logistical limitations and extensive number of experiments, certain experiments were conducted on select samples considering the characteristics of the sampling location. These characteristics include the level of As contamination, presence of phosphate, and sediment overall adsorptive capacity. Additional information about the study site is also available elsewhere (Hafeznezami et al., 2016a, b).

2.1. Study site and sample collection

The study site (Fig. 2), located in New England, USA, is a former manufacturing facility where leaching of high pH industrial waste sludge from unlined surface impoundments has led to mobilization of naturally occurring As. Mobilized As in the groundwater is predominantly present as the oxidized form As(V). Historical groundwater quality data show elevated levels of As(V) (up to 2 mg/L), phosphate (up to 14 mg/L) and high pH (up to 10.5). Currently, the As(V) concentrations range from 140 μgL^{-1} to 800 μgL^{-1}. The high pH waste sludge is believed to have contained phosphate-based detergents and chelating agents as well as copper and other plating metals. The source of As(V) in the groundwater is attributed mainly to the desorption and leaching from native solid phases into groundwater due to increased pH and phosphate concentrations (Hafeznezami et al., 2016b).

Sediments from seven locations, Sites 5, 6, 7, 9, 11, 12, and 13 were used in this study (Fig. 2). Sediment samples were collected in 2014–2015 and shipped to UCLA in sealed bags on ice. All sediment and groundwater samples were stored refrigerated (4 °C) in the dark until use. Sample collection details and characterization of the sediments have been described in detail elsewhere (Hafeznezami et al., 2016a). Following collection of soil samples, groundwater samples were collected using low-flow sampling techniques from wells co-located with the soil samples. The wells were purged using a peristaltic pump with dedicated LDPE tubing. Pumping rates were controlled to minimize drawdown to approximately 1 foot or less. Temperature, pH and specific conductance were monitored during purging until these parameters stabilized. Groundwater samples were collected in clean, unpreserved 250 mL plastic bottles and refrigerated until experimental set-up of batch acidification and column experiments as described in the following sections. Preserved samples were analyzed for As and other elements by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

2.2. Analytical methods

All lab-ware were soaked in 1.2 N HCl for at least twelve hours and rinsed with Milli-Q (18MΩ) water five times prior to use. All solutions were prepared using Milli-Q water purified by a NANOpure deionization system. Sediments in batch suspensions were separated from solutions by centrifuging at 7800 RPM for 15 min and supernatants were syringe-filtered through 0.45 μm disposable MCE filters (EMD Millipore). All samples for As analysis were preserved upon collection (2%v/v HNO_3) and refrigerated (4 °C) if not immediately measured.

All chemicals used were of laboratory reagent grade. Arsenic added to factorial and isotherm experiments was prepared from $Na_2HAsO_4 \cdot 7H_2O$ (Sigma Aldrich). The pH values were adjusted in all experiments using 0.1 N HCl and NaOH. HEPES buffer was used to maintain a constant pH throughout the course of the experiments. HEPES has been shown to have negligible influence on As adsorption processes (Kanematsu et al., 2010). pH of solutions was measured using an Acumet Basic AB 15 pH meter, calibrated regularly with standard pH buffer solutions (4, 7, and 10). For batch studies, the experimental tubes were shaken using rotisserie rotators for the specified duration at 8 rpm. Based on previous kinetic adsorption studies, reaction time of 7 days was selected for reaching equilibrium in batch experiments (Hafeznezami et al., 2016a).

2.2.1. Groundwater quality

Preserved site groundwater samples were analyzed for As and other elements by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), conducted at the School of Public Health at UCLA according to standard methods.

Previous studies showed that As(V) is the predominant species in the oxidizing groundwater at this site (Hafeznezami et al.,

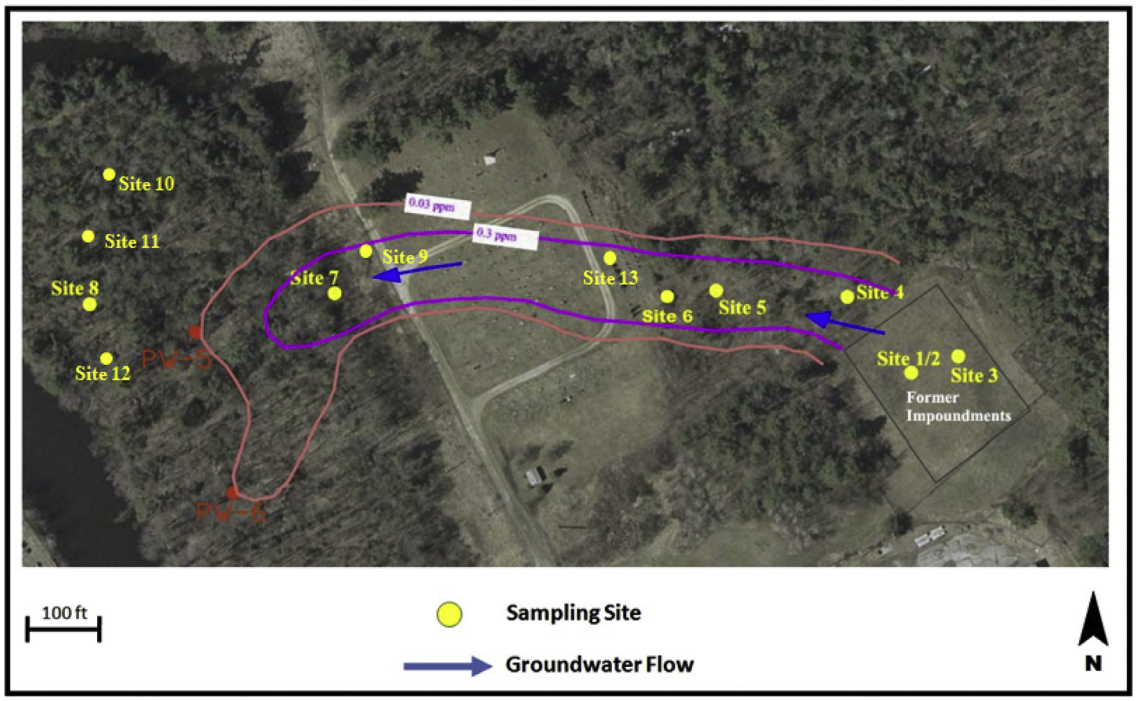

Fig. 2. Map of the study site showing the industrial waste impoundment location, sampling sites, and the contours of the dissolved As(V) concentration.

2016b); therefore, total As measurement is assumed to represent As(V) concentrations. During batch experiments, total As concentration in filtered solutions was measured by Graphite Furnace Atomic Absorption Spectrometry (GFAAS) (Perkin Elmer AAnalyst 700) with an electrodeless discharge lamp (EDL). 20 μL of sample plus 5 μL of matrix modifier ($Pd(NO_3)_2$ and $Mg(NO_3)_2$) was used for each measurement. The instrument was calibrated on a daily basis with minimum of five standard solutions (5–100 μg/L) prepared from stock solution obtained from Perkin Elmer. The analyses were conducted in triplicate and the relative standard deviations of measurements were consistently below 5%.

Fe(II) measurements were done spectrophotometrically using the Ferrozine method (Stookey, 1970; Lovley and Phillips, 1986) at 562 nm. Samples were sent to University of California Davis Analytical Laboratory to be analyzed for Ca using Inductively Couples Plasma Atomic Emission Spectrometry (ICP-AES).

2.2.2. Site sediment characterization

Previously conducted X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses of the sediments indicated that site sediments are predominately quartz and feldspars; all other phases were below the quantifiable limit of detection (Hafeznezami et al., 2016a).

2.3. Remediation factorial experiments-testing effect of pH, Ca, and Fe

The effects of three parameters (pH, Ca, Fe) on retention of As(V) on sediments from six sites (Sites 5, 6, 7, 9, 11, 13) were studied in a batch factorial design to quantify and assess the level of improved removal rate using different variations of these parameters. A constant concentration of As (2.5 mg/L) was added to sediment suspensions in duplicates made up of mixing 9 g of sediment and 30 mL of solution (0.3 kg/L ratio). This choice of mixing ratio was made to maximize the amount of used sediment to the extent possible in a batch setting. Three concentrations of phosphate (0.03, 0.7, 2 mg/L) were used in the experiments and were selected to be representative of levels observed in site groundwater.

Each of the three factorial parameters (pH, Ca, Fe) were varied at two specified levels described below, while the levels of phosphate and As were kept constant over the course of each experiment. pH values of 7 and 9 were used to represent background and elevated pH conditions at the study site. Fe concentrations of 1 and 20 mg/L and Ca concentrations of 1 and 50 mg/L were used to represent low and high concentrations, respectively. Concentrations of Ca and Fe were chosen based on preliminary calculations and considered the feasibility of achieving similar concentrations in the field. Each factorial condition was tested in duplicate.

2.4. Batch adsorption experiments-testing the effect of Ca

Batch adsorption experiments for studying the effect of Ca were conducted by mixing 5 g of sediment from Site 9 and Site 13 and background electrolyte solution (0.1 M NaCl, 5 mM HEPES) with a 100 g/L ratio as described elsewhere (Hafeznezami et al., 2016a, b). Site 9 and 13 sediment was used to represent sites with high As concentrations in the groundwater where such remediation scenario could be considered. Final Ca concentrations of 1, 50, and 100 mg/L were achieved in suspensions by adding $CaCl_2$ salt. These values were selected considering the natural range of groundwater Ca concentrations at the study site. Suspensions were mixed overnight and pH was adjusted to 7 prior to spiking with As(V). The pH of suspensions were monitored and adjusted as needed on a daily basis.

Experimental tubes were shaken using rotisserie rotators for the specified duration at 8 rpm. Based on previous kinetic adsorption studies, a reaction time of seven days was selected for reaching equilibrium (Hafeznezami et al., 2016a). On day seven, the solutions were centrifuged and filtered and analyzed for dissolved As(V). A mass balance approach was applied to calculate concentrations adsorbed.

2.5. Sediment column experiments-testing the effect of Ca and Fe

Column studies were conducted using glass columns (Spectra/Chrom) with 0.9 cm inner diameter and 15 cm length. Sediment samples were air-dried and passed through 2 mm sieve prior to packing the columns. Sediment was added in approximately 1 cm increments and compacted by dropping a custom made pestle (weighing 16 g) ten times.

Assuming 2.65 g/cm^3 particle density for sand, the mass of sediments in the columns was used to calculate the porosity achieved by this packing method. Tracer studies using a dye (Brilliant Blue FCF) were conducted on control columns using the corresponding sediment type to verify the porosity calculations. All determined porosities were below 5% margin of error. Table 1 lists the achieved porosity values and relevant column characteristics used in this study.

Peristaltic pumps were run for a week on a control (packed) and empty column to calibrate the flow rate, prior to experimental initiation. The minimum achievable flow rate of 0.01 mL/min was used for running the columns with groundwater in order to ensure the adequate residence time needed for sorption kinetics.

For consistency, equal length of tubing was used for all columns and all columns were positioned at identical heights. Columns were fed with groundwater collected from the study site (Table 2) continuously and upward at a constant 0.6 mL/h rate at the ambient temperature (~25 °C). Input solutions were kept refrigerated in the dark and were added to 50-mL reservoirs on a daily basis. Solutions were pumped through the columns using high accuracy digital Masterflex pumps and compatible L/S 13 and 14 chemical resistant Tygon tubing.

Columns and influent reservoirs were covered with aluminum foil to prevent light exposure and minimize the possibility of any photochemically induced reactions. The effluent of columns was collected and analyzed for different water quality parameters at six-hour intervals (approximately 1–1.2 pore volumes) on a daily basis for the duration of experiments. Collected samples were filtered (0.45 m) and a constant aliquot was added to pre-acidified (2% HNO_3) micro-centrifuge tubes for subsequent analysis with GFAAS. Alkalinity, conductivity, dissolved oxygen (DO), pH and temperature of the effluents were monitored for duration of the experiments.

Two rounds of column experiments were completed. In the first round, the sorption and transport of As on contaminated sediments was studied. In the second, the sorption and transport of As on uncontaminated sediments was studied. Duplicate columns were set up and tested for each treatment. Column experiments were run in three phases. The columns were first equilibrated with the corresponding un-contaminated groundwater for 20 pore volumes to achieve an initial equilibrium condition. Next, the input solutions were switched to the As-contaminated groundwater collected from Site 7. Flowing contaminated groundwater collected from within the plume through columns packed with un-impacted sediments will simulate the scenario of the contaminated groundwater reaching the targeted sites. Finally, at approximately 50 pore volumes after the occurrence of As breakthrough, a second input line containing either Ca (Round One and Round Two) or Fe(II) (Round One Only) was added to each column. The amendment chemicals were added with 10% flow rate of groundwater and the level of dilution applied to the groundwater composition was taken into account for data analysis. In both Rounds One and Two, pH of Fe(II) solution in the feed reservoir was adjusted to 2.75 in order to avoid premature oxidation before entering the columns. After the conclusion of the experiments, sediments were extruded from the columns in 2 cm increments and analyzed for total solid phase As and Fe.

2.5.1. Round 1-sites 11 and 12, testing effect of Ca and Fe addition

In the first round of experiments, sorption and transport of As within columns packed with un-contaminated sediments from Site 11 and 12 was studied. The experiments were run in three phases as described above. In the final phase, Ca (added as $CaCl_2$ salt to columns 11A and 12A) or Fe(II)(added as$FeCl_2$ salt to columns 11B and 12B) was added to each column. The final concentrations of Fe(II) and Ca in the mixture entering the columns were 10 and 50 mg/L respectively.

2.5.2. Round 2-sites 5 and 7, testing effect of Fe addition

A second round of experiments was conducted testing contaminated groundwater from Sites 5 and 7. Contaminated groundwaters from Sites 5 and 7 were run through columns packed with corresponding sediments as described above. Remediation by addition of a second influent stream containing only Fe(II) (20 mg/L) was studied.

2.6. Data analysis and modeling

An analysis of variance (ANOVA) was applied to analyze the differences among removal rate means for the different batch experiments. IBM SPSS Statistics software version 22 was used for all statistical analyses.

Geochemical modeling software, PHREEQC (Parkhurst and Appelo, 2013) was used to calculate the saturation indices for Ca-arsenate and Ca-phosphate precipitates in the batch and column. The miteq.v4 database was updated with metal arsenate solubility product constants from the literature (Martínez-Villegas et al., 2013).

3. Results

3.1. Groundwater quality

Groundwater quality for Sites 5, 7, 11, and 12 are presented in Table 2. Sites 11 and 12 (uncontaminated sites) are beyond the limits migration of the arsenic plume and dissolved As(V) and phosphate concentrations in these sites were below levels of detection. pH values at these sites were below 8 and similar to

Table 1
Column physical properties.

Column	Sediment Mass (g)	Porosity (%)	Solid/Solution (kg/L)	Residence Time (h)	Dry bulk density (g/cm^3)	Flow (mL/h)
S-11A	16.87	38.2	4.29	6.56	1.64	0.60
S-11B	17.39	36.3	4.65	6.23	1.69	0.60
S-12A	17.59	35.6	4.80	6.10	1.71	0.60
S-12B	17.89	34.5	5.04	5.92	1.74	0.60
S-7A	20.04	26.6	7.32	4.56	1.95	0.60
S-7B	20.14	26.2	7.46	4.50	1.96	0.60
S-5A	16.65	39.0	4.14	6.69	1.62	0.60
S-5B	16.44	39.8	4.01	6.83	1.60	0.60

Table 2
Groundwater quality data.

Site	pH	As (μg/L)	Fe (μg/L)	PO_4-P (mg/L)	Ca (mg/L)	Na (mg/L)	Al (mg/L)
S-5	9.6	60	130	1.4	0.2	49.7	0.3
S-7	8	510	190	8.8	1.2	105	0.1
S-11	7.1	<5	10	<0.1	23.1	8	0.1
S-12	7.5	<5	300	<0.1	101	88.6	0.2

background conditions observed upstream of the plume.

Site 7 is located within the plume downgradient of the original source of contamination. Aquifer material at this site is mainly classified as sand and gravel. Elevated As(V) and phosphate concentrations (As = 510 μg/L, P = 8.8 mg/L) were observed.

Site 5 is located upgradient in the contaminated plume (near the impoundments). Elevated As(V) and phosphate concentrations were also observed at this site. Concentrations observed appear to be dropping steadily over time compared to levels measured in 2011 (unpublished report) from 145 to 61 μg/L for As(V) and 6.05 to 1.4 mg/L for phosphate, respectively. In contrast, pH has remained consistently elevated-levels measured in this study were consistently above 9 and were similar to those measured in 2011. Ca concentrations measured in the groundwater from these sites were relatively lower than the concentrations observed in the unimpacted area (Sites 11 and 12).

3.2. Remediation factorial experiments-testing effects of pH, Ca, and Fe

Removal rates observed in all batch treatments are presented in Table 3.

An analysis of variance (ANOVA) was applied to analyze the differences among removal rate means for the different batch experiments. Overall, the treatment (variation of Ca, Fe, and pH) significantly affected the removal rate relative to the untreated control samples ($P < 0.001$). Removal efficiency was significantly increased for the effect of Ca ($P < 0.001$), Fe ($P < 0.001$), pH ($P < 0.05$), and PO_4^{3-} ($P < 0.05$). The highest As(V) removal efficiency was observed for the treatment that combined low pH, high Fe, and high Ca concentrations (see Table 3, Fig. 3). Among the factors tested, Fe amendment (20 mg/L) and Ca amendment (50 mg/L) showed the greatest effect on removal rates by increasing sorption by an average of 43% and 32% ($P < 0.001$), respectively. pH adjustments resulted in the smallest increase in additional sorption (18% on average).

In contrast, the level of phosphate present in the system did not significantly affect the increased removal rate due to the Ca amendment ($P = 0.13$). Ca is likely increasing the observed removal rates through improvement of the surface adsorption by modifying the surface charge of sediments rather than through precipitation of phosphate.

No significant difference in removal rate was observed among the different sediments tested (Sites 5, 6, 7, 9, 11, and 13). However, there was a positive correlation ($R^2 = 0.87$, $P = 0.01$) between increased removal by chemical amendments and the Langmuir-derived adsorption capacity of the tested sediments from previous isotherm experiments (Hafeznezami et al., 2016a).

3.3. Batch adsorption experiments-testing effect of Ca

The impact of Ca on As(V) adsorption at Site 9 and 13 was tested. Adsorption over time is presented in Fig. 4. The Langmuir isotherm model was applied to the adsorption experimental data in order to estimate the adsorption capacity of sediments for As(V) under different levels of Ca. Higher levels of Ca (50 mg/L and 100 mg/L) increased adsorption. The maximum adsorption capacity (S_t), derived from non-linear fitting of Langmuir model to adsorption data, was increased between 26 and 46% for the highest level of Ca treatment. These results provide further evidence for the increase in adsorption capacity of sediments when amended with Ca as observed in the factorial experiments.

3.4. Sediment column experiments

3.4.1. Round 1-sites 11 and 12, testing effect of Ca and Fe addition

Arsenic sorption and transport was tested on sediment collected from Sites 11 and 12 (uncontaminated sediment site). Columns 11A and 11B effluents showed breakthrough of As(V) after 5 pore volumes (Fig. 5). The concentration of As(V) in the effluents exceeded the levels present in the influent groundwater by over 280 μg/L, which is an increase of 56%. This suggests that the incoming groundwater induced desorption of As(V) from the sediments. The As(V) concentrations dropped to an average of 540 μg/L after 12 pore volumes and remained relatively unchanged until the start of chemical amendment after60 pore volumes.

In column 12A and 12B breakthrough occurred after only 1 pore volume and the effluent As(V) reached maximum concentration of 600 μg/L. The difference observed between the attenuation capacity of sediments Site 11 and Site 12 is in agreement with the previous adsorption isotherm results indicating that Site 11 has higher adsorption capacity than Site 12 (Hafeznezami et al., 2016a). Unlike the trends observed for As(V), no desorption of phosphate from sediments was observed and the effluent levels did not exceed the influent concentrations. In both columns for Site 11 and Site 12, the effluent phosphate concentrations did not significantly exceed the influent concentrations for the duration prior to start of the chemical amendment.

The initial desorption of As(V) from sediments is also observed for Site 5 and Site 7 columns with As(V) concentrations in the effluents reaching 250 and 670 μg/L respectively (Fig. 6). For these two sites no natural attenuation of contaminant by sediments was observed and the breakthrough of As(V) occurred immediately after only 1 pore volume.

Addition of Ca in columns 11A and 12A yielded similar results. After Ca amendment, initial As(V) concentrations in the effluent dropped, suggesting an improvement via surface adsorption. However, after certain number of pore volumes (19 in 11A and 8 in 12A) As(V) concentrations returned to levels observed before the amendment. Effluents from column 12A experienced an additional drop in As(V) concentrations lasting for nine pore volumes before returning to levels similar to groundwater influent, indicating lack of retention in the columns. The pH in effluents of Site 11 and Site 12 columns remained relatively unchanged during the course of the experiments (pH of 8.2–8.4).

The observed results for As(V) coincide with the gradual increase of Ca concentrations in the column effluents up to 50 mg/L indicating lack of further Ca adsorption on the sediment surfaces.

The initial improvement was also observed for phosphate, however the effluent phosphate concentrations remained lower than the baseline until the last pore volume sampled indicating that the Ca amendment was still effective in improving retention rates.

Table 3
Results of factorial remediation experiments. Subscripts 0 and 7 indicate the concentration initial and at equilibrium after 7 days. Enhanced removal percentages are calculated relative to control samples. (*ND = not detected).

Sediment Site	Sample ID	pH	Fe (mg/L)	Ca (mg/L)	P_0 (mg/L)	As_0 (μg/L)	As_7 (μg/L)	As Removal (%)	P_7 (mg/L)	Enhanced Removal (%)
S-5	1	9	20	50	0.7	2500	75.2	97.0	0.1	69.6
	2	9	20	1	0.7	2500	191.7	92.3	1.1	22.4
	3	9	0.5	50	0.7	2500	201.8	91.9	0.9	18.3
	4	9	0.5	1	0.7	2500	259.4	89.6	1.0	−5.0
	5	7	20	50	0.7	2500	20.8	99.2	0.0	91.6
	6	7	20	1	0.7	2500	115.9	95.4	0.4	53.1
	7	7	0.5	50	0.7	2500	143.1	94.3	0.6	42.1
	8	7	0.5	1	0.7	2500	245.1	90.2	1.2	0.8
	Control	9.2	–	–	0.7	2500	247.1	90.1	1.3	0.0
S-6	1	9	20	50	0.03	2500	137.9	94.5	ND	79.4
	2	9	20	1	0.03	2500	195.1	92.2		70.8
	3	9	0.5	50	0.03	2500	409.8	83.6		38.7
	4	9	0.5	1	0.03	2500	618.9	75.2		7.4
	5	7	20	50	0.03	2500	81.9	96.7		87.7
	6	7	20	1	0.03	2500	101.0	96.0		84.9
	7	7	0.5	50	0.03	2500	238.5	90.5		64.3
	8	7	0.5	1	0.03	2500	333.3	86.7		50.1
	Control	8.8	–	–	0.03	2500	668.3	73.3		0.0
S-7	1	9	20	50	2	2500	155.5	93.8	0.0	85.5
	2	9	20	1	2	2500	665.3	73.4	0.1	37.9
	3	9	0.5	50	2	2500	462.3	81.5	0.0	56.8
	4	9	0.5	1	2	2500	1036.8	58.5	0.6	3.2
	5	7	20	50	2	2500	43.3	98.3	0.0	96.0
	6	7	20	1	2	2500	88.3	96.5	0.0	91.8
	7	7	0.5	50	2	2500	319.0	87.2	0.0	70.2
	8	7	0.5	1	2	2500	979.9	60.8	0.3	8.5
	Control	8.5	–	–	2	2500	1070.9	57.2	0.5	0.0
S-9	1	9	20	50	0.7	2500	0.0	100.0	0.0	100.0
	2	9	20	1	0.7	2500	17.0	99.3	0.0	94.7
	3	9	0.5	50	0.7	2500	47.2	98.1	0.0	85.4
	4	9	0.5	1	0.7	2500	304.7	87.8	0.4	5.5
	5	7	20	50	0.7	2500	0.0	100.0	0.0	100.0
	6	7	20	1	0.7	2500	0.0	100.0	0.0	100.0
	7	7	0.5	50	0.7	2500	24.1	99.0	0.0	92.5
	8	7	0.5	1	0.7	2500	228.5	90.9	0.2	29.2
	Control	8.4	–	–	0.7	2500	322.6	87.1	0.0	0.0
S-11	1	9	20	50	0.03	2500	23.5	99.1	ND	94.5
	2	9	20	1	0.03	2500	53.2	97.9		87.6
	3	9	0.5	50	0.03	2500	83.1	96.7		80.6
	4	9	0.5	1	0.03	2500	350.0	86.0		18.1
	5	7	20	50	0.03	2500	11.2	99.6		97.4
	6	7	20	1	0.03	2500	12.9	99.5		97.0
	7	7	0.5	50	0.03	2500	23.7	99.1		94.4
	8	7	0.5	1	0.03	2500	103.7	95.9		75.7
	Control	7.5	–	–	0.03	2500	427.5	82.9		0.0
S-13	1	9	20	50	1.5	2500	24.0	99.0	0.0	90.5
	2	9	20	1	1.5	2500	149.7	94.0	0.5	40.8
	3	9	0.5	50	1.5	2500	193.6	92.3	0.5	23.4
	4	9	0.5	1	1.5	2500	272.5	89.1	1.1	−7.8
	5	7	20	50	1.5	2500	12.8	99.5	0.0	94.9
	6	7	20	1	1.5	2500	121.3	95.1	0.0	52.0
	7	7	0.5	50	1.5	2500	160.5	93.6	0.3	36.5
	8	7	0.5	1	1.5	2500	229.0	90.8	0.9	9.4
	Control	9.2	–	–	1.5	2500	252.8	89.9	0.9	0.0

Treatment of columns with Fe(II) showed an initial stage of fluctuations (20 pore volumes in 11B and 18 pore volumes in 12B) in As(V) effluent concentrations, followed by a gradual increase in removal until the last pore volume sampled.

3.4.2. Round 2-sites 5 and 7, testing the effect of Fe addition

Arsenic sorption and transport was tested in uncontaminated sediments collected from sites 5 five and seven. Treatment of column 5A with 20 mg/L of Fe(II) resulted in reduction of As(V) effluent concentration to below the EPA drinking MCL of 10 μg/L after six pore volumes. Column 5B experienced loss of effluent volume after 5 pore volumes due to clogging. Columns 7A and 7B achieved an average removal rate of 62% of As(V) after 5 to 9 pore volumes.

Effluent pH before the amendments was between 8.3 and 8.4 and was subsequently lowered to between 7.5 and 7.8 following the start of amendments. These results imply the presence of major pH buffering capacity within the tested sediments. Other factors such as CO_2 outgassing from the groundwater samples due to the difference between the partial pressures in an aquifer and the laboratory atmosphere could also be partially responsible for the observed increase in the pH levels of groundwater.

Effluents were measured continuously for presence of Fe(II). Concentrations observed were below the detection limit (<1 mg/L), indicating that the added Fe(II) is mostly oxidized after mixing with the groundwater at the injection port and through the columns. Moreover, adsorption of Fe^{2+} ions onto mineral surfaces could also explain the lag period following the start of amendment.

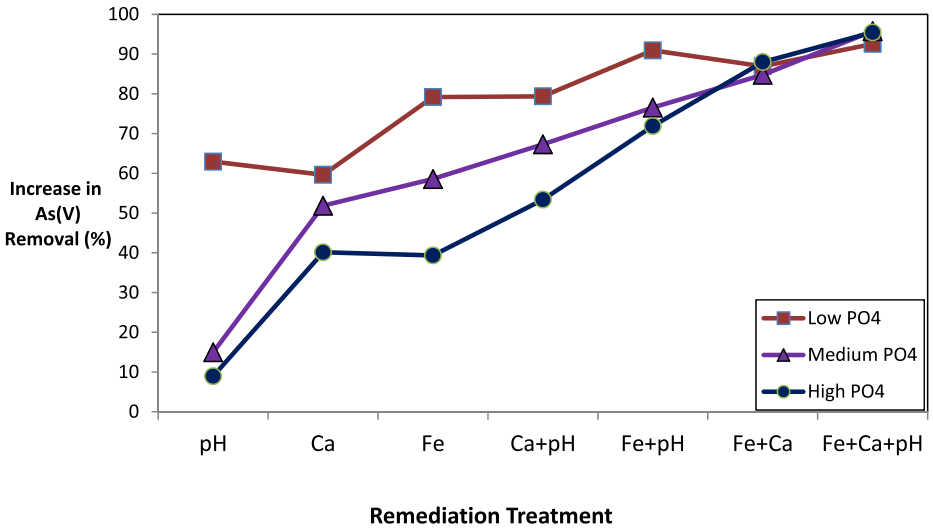

Fig. 3. Average effect of remediation treatments on increased As(V) removal relative to control samples from batch factorial tests under three levels of phosphate (0.03, 0.7, 2 mg/L for low, medium, and high respectively). The x-axis labels indicate the category of remediation treatments (lowering pH, adding Fe, and adding Ca).

4. Discussion

This study investigated the potential for adjusting levels of pH, Ca, and Fe and to enhance the attenuation capacity of sediments for As (V) using batch and column experiments.

4.1. Attenuation mechanisms

Overall, Fe amendment had the highest individual impact on As(V) levels, likely resulting from precipitation and formation of additional sorption sites. Ca amendment and pH conditions were also effective at enhancing the attenuation capacity of the tested sediments, and performance depended on treatment conditions.

Ca amendments were found to significantly improve the adsorption capacity for As(V) under varying conditions. Factorial experiments demonstrated that while at low PO_4^{3-} conditions, pH adjustment is more effective at As(V) retention, at higher phosphate levels, Ca amendment becomes more effective.

Three main mechanisms can be hypothesized to explain the effect of Ca amendment on As(V) assimilation. Firstly, Ca^{2+} cation adsorption onto solid surfaces neutralizes the negative surface charges, hence increasing the affinity of surface adsorption of the negatively charged arsenate species. The second possible mechanism is through super-saturation and consequent precipitation of Ca-phosphate phases, reducing the competition and therefore could increase As adsorption. The third possible mechanism is formation of Ca-arsenate precipitates. However, geochemical modeling results indicate that neither the indices for Ca arsenate of Ca phosphate precipitates are supersaturated, ruling out the possibility of Ca influencing the results through precipitation reactions. These observations indicate that precipitation of Ca containing phases is not the likely mechanism responsible for improved As(V) removal.

Analyzing the adsorption isotherm results in absence of competing ions such as phosphate illustrate that addition of Ca significantly improves the adsorption capacity. This beneficial impact can be explained by either the charge-neutralizing effect of the Ca^{2+} cation on surface sites (consequently enhancing the affinity for negatively charged As(V) oxyanion) or the formation of ternary complexes. The additional adsorption capacity observed increases with increasing As(V) concentrations. These results indicate that there is likely a threshold amount of Ca needed to modify the solid surface charges to a level that compensate the potential competing effect of Ca. Other studies have also shown stabilizing effect of Ca on As in solid phases (Camacho et al., 2009; Martínez-Villegas et al., 2013).

4.2. Column amendments

Column results for Site 11 and 12 show an initial fast rate As(V) desorption from these historically un-impacted sediments followed by a slower, steady desorption rate until the start of remediation. The observed desorption is mainly due to the high pH and PO_4^{3-} characteristics of the influent water. This finding is important for understanding the mechanisms of historical contamination at this site and demonstrate that the original source of As in the plume was in fact the naturally occurring As in the sediments released due to alkaline and competitive desorption processes.

While the As(V) breakthrough occurs after only a few pore volumes, phosphate maintains a larger and more steady level of attenuation both before and after the chemical amendments.

Different levels of sorption were observed after the chemical amendments in the columns, with maximum removal efficiencies achieved for As(V) ranging between 39 and 91% (Fig. 7). Amendment with Fe(II) resulted in 50–91% As(V) removal rates in the columns compared to 39–79% achieved by Fe(III) amendment in batch factorial experiments at a much lower PO_4^{3-} ranges. Removal rates achieved by Ca amendment were comparable between the column and batch factorial experiments.

It can be inferred from the results that two factors could work against the effective removal of As(V) by Fe(II) amendment. The first factor, given the relatively short residence time achieved in the columns, is the kinetics of oxidation and precipitation of Fe oxides that could explain the observed lag in the experimental results. However, kinetics may be a minor factor in the field conditions because of the significantly slower flow velocity of groundwater. The second factor affecting the removal rates is the natural pH buffering of the sediments which is evident in the stable alkaline conditions of the column effluents. The pH values of column effluents in this study are controlled by kinetic dissolution of calcite and the buffering of pH by surface sites. Arsenate is less strongly adsorbed at higher pH values due to electrostatic repulsion.

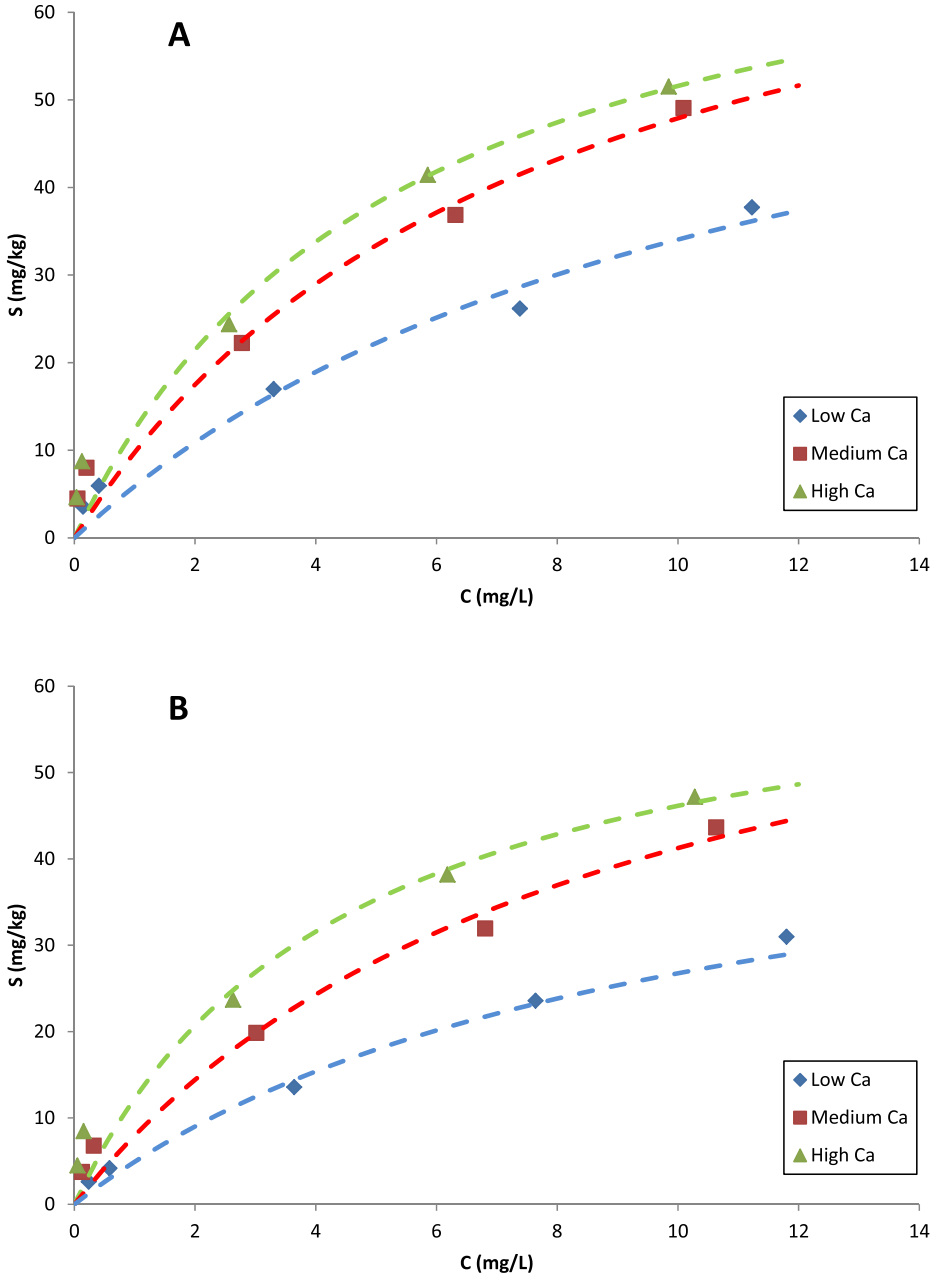

Fig. 4. Adsorption isotherm results of As(V) for three levels of Ca (Low = 1 mg/L, Medium = 50 mg/L, High = 100 mg/L) at A) Site 9, and B) Site 13.

Therefore, the extent to which pH values can be lowered will greatly influence the As(V) retention by sediments as seen in the factorial experiments.

4.2.1. Column Ca amendments

Calcium amendment initially improved the adsorption rate in columns. However, this impact is temporary for As(V) and the increased attenuation capacity becomes exhausted after certain number of pore volumes. The gradual increase in column effluent Ca concentrations coincide with the increase in As(V) back to the influent levels indicating that once surface sites are saturated by Ca and the maximum adsorption on the surfaces occur, the incoming flux of high pH and PO_4^{3-} solution begins neutralizing the Ca effect and outcompeting As(V).

4.2.2. Column Fe amendments

Fe(II) application in the current study resulted in maximum removal rates between 50 and 91%. The Fe amendment yielded favorable results for As(V) removal in Site 11 and Site 12 columns after a significant number (20) of pore volumes. This could be due to the lack of sufficient reaction time for adsorption of As(V) on the freshly formed Fe phases. The absence of Fe(II) in the column effluents indicates complete oxidation taking place within the columns, however the formation of Fe oxide phases and adsorption of As(V) may require longer reaction times than the average residence time of solution in the columns. In columns Site 5 and Site 7 with application of 20 mg/L of Fe(II), the enhanced attenuation was observed immediately after the amendment started, however this led to reduced flow through the columns. This amendment was successful in lowering the As(V) concentration in Site 5 from 60 μg/

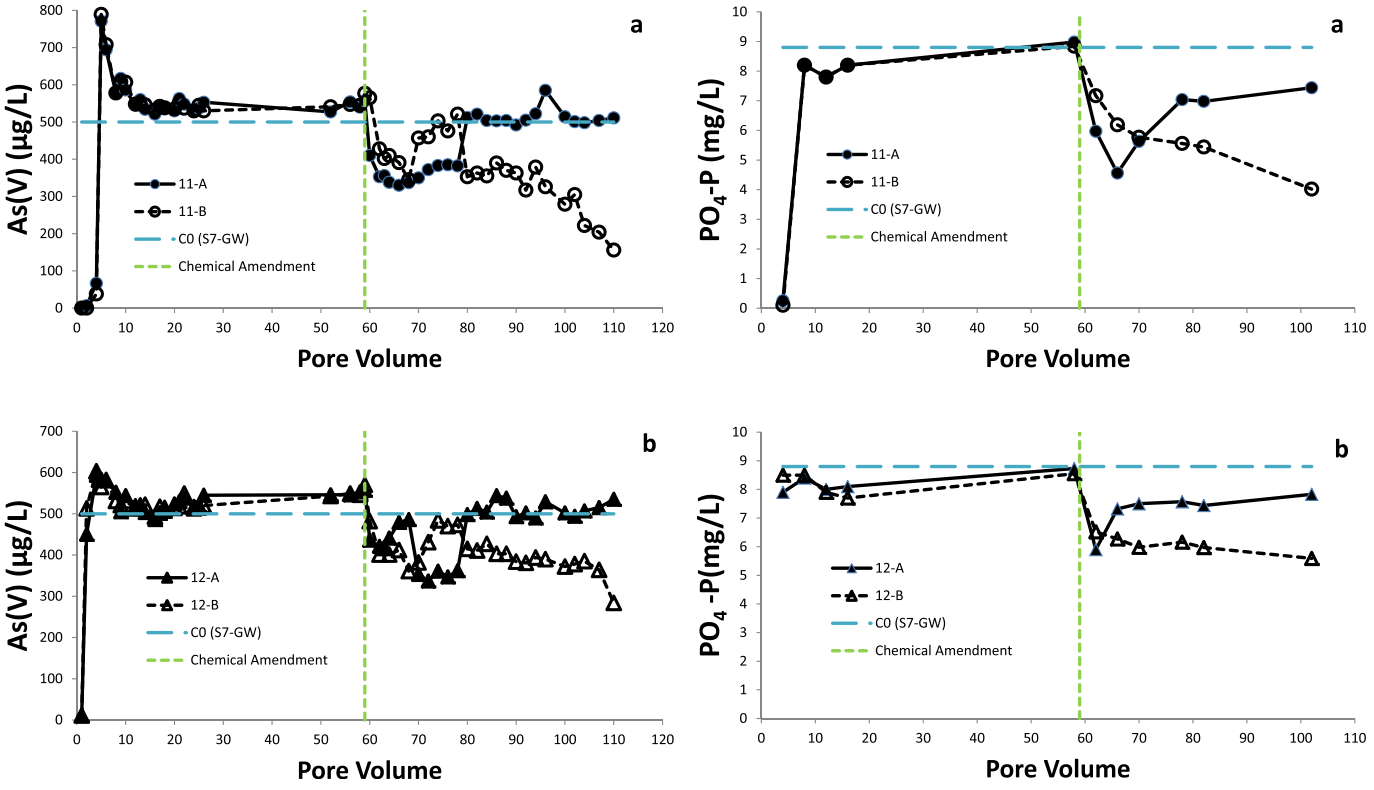

Fig. 5. Concentrations of As(V) and PO_4-P in the effluents of columns packed with un-impacted sediments. a) Site 11, and b) Site 12. Closed symbols represent columns amended with 50 mg/L Ca (11A & 12A) and open symbols represent columns amended with 10 mg/L Fe(II) (11B & 12B). The horizontal dashed lines depict the concentrations in influent contaminated groundwater and the vertical dashed lines indicates the start of chemical amendment.

L to below 10 µg/L.

It should be noted that the long term effectiveness of in-situ remediation by inducing precipitation of Fe oxides is dependent on variety of geochemical factors affecting the newly formed phases. Chemical stability of these phases is controlled by the redox conditions present in the aquifer. Presence of electron donors such as organic matter could lead to reductive dissolution of host sites and release of retained As(V) back into solution. Aging and transformation of freshly formed amorphous phases (e.g. ferrihydrite) to more crystalline (e.g. goethite) is a phenomenon that causes decrease in the specific surface area of Fe oxides and consequently loss of adsorptive capacity.

5. Conclusions

Factorial remediation results show that the combination of low pH, high Fe and high Ca results in highest level of As(V) removal from solution phase compared to control samples. This effect however, decreases with the increase in the phosphate concentrations due to the competition factor.

In this study, beneficial effect of Ca amendment on As(V) sorption was observed in batch factorial and isotherm experiments, as well as in a limited way in the column studies. Calculated SI values from PHREEQC indicate that none of the Ca-arsenate or Ca-phosphate species are supersaturated, therefore ruling out the possibility of precipitation of these phases as an explanation of the results. This work is one of the few studies that clearly show the beneficial effect of Ca addition on improving the immobilization of As. Future studies are needed to investigate the interactions between Ca and As(V) on the surfaces of minerals in more detail.

The results of the column experimental work conducted in this study show that immobilization of As(V) in a contaminated aquifer is possible by chemical amendments aimed at increasing the natural attenuation capacity of the aquifer materials through enhancing the sorption mechanisms responsible for removing As from solution. Further work is needed for transferring these results to a larger scale and eventually implementation in the field.

Iron oxides are well-known to have significant affinity for adsorbing As from solution phase via forming inner-sphere surface complexes. These phases are commonly present and widely distributed in sediments and have been used extensively for treating contaminated waters. Addition of Fe containing compounds leading to precipitation and formation of oxide/hydroxide coatings in the aquifer matrix could enhance the natural attenuation by creating additional sorption sites and increasing the capacity for immobilization of contaminants such as As. However, the kinetics of Fe(II) oxidation and precipitation of Fe(III) phases, as well as kinetics of As(V) adsorption onto the freshly formed solids could be a major factor limiting the removal rates.

Given the vast number of contaminated groundwater cases nationally and globally, there is a growing need for alternative treatment strategies that are cost-effective, efficient, and effective.

In-situ remediation of As-contaminated groundwaters can be a viable alternative to the conventional above ground treatment methods. Any efforts to facilitate the immobilization of As in contaminated groundwater systems need to take into account the different parameters controlling the attenuation processes such as pH, redox potential, competing ions, soil chemical and physical characteristics. Results of this study can be used to assess the natural capacity of sediments in hindering the initial transport of As through un-impacted sites as well as the efficiency of applying in-situ remediation through chemical amendments.

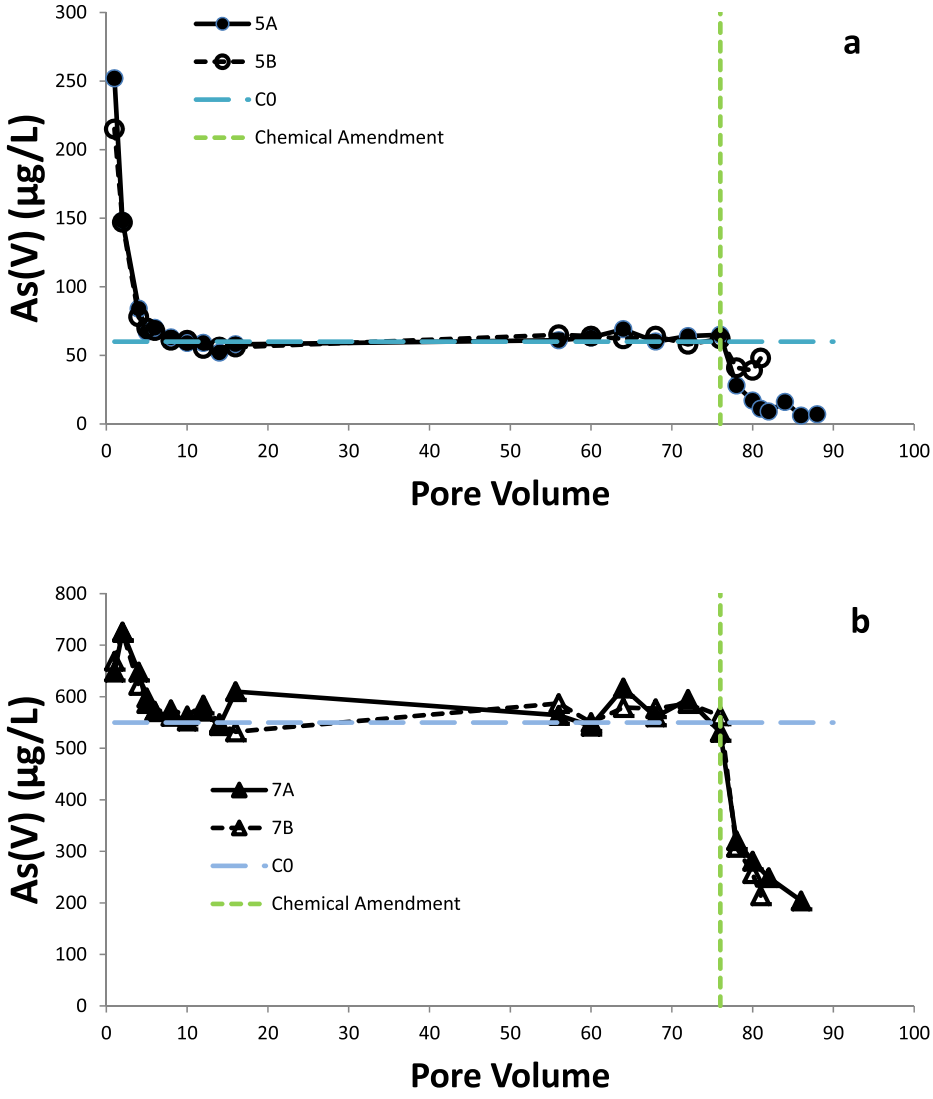

Fig. 6. Concentrations of As(V) the effluents of columns packed with impacted sediments. a) Site 5, and b) Site 7. Closed and open symbols represent the duplicates amended with 20 mg/L Fe(II). The horizontal dashed lines depict the concentrations in influent contaminated groundwater and the vertical dashed lines indicates the start of chemical amendment.

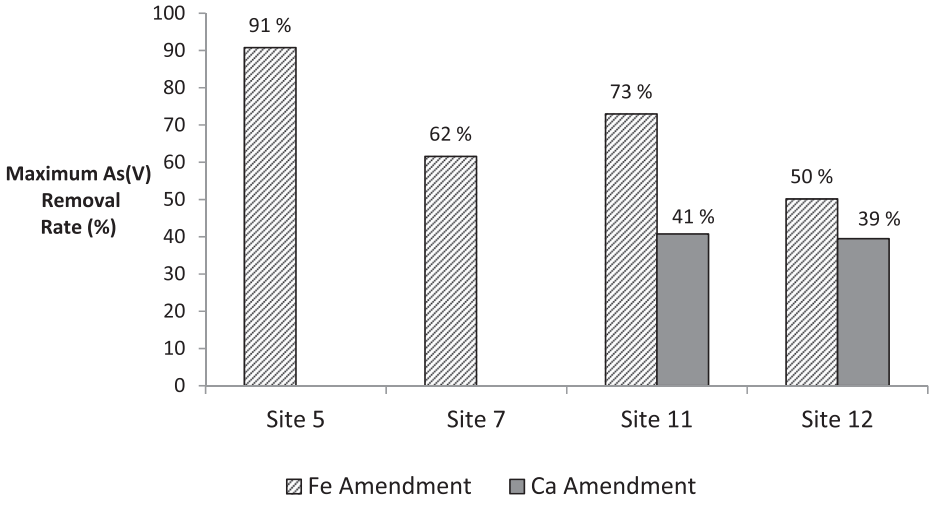

Fig. 7. Summary of maximum removal rates (%) for As(V) achieved in columns with chemical amendments.

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